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WHAT CAN WE LEARN FROM RELAXATION MEASUREMENTS OF A LASER-PERTURBED ATMOSPHERE? A MODELING STUDY

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ABSTRACT

The chemical kinetic aspects of a transient increase in OH and HO₂ by several orders of magnitude are explored in three model tropospheres. This chemical kinetic modeling effort was undertaken to support the operation of a pump-and-probe LIDAR instrument. A powerful excimer laser pulse perturbs the troposphere after which its relaxation back to steady state is examined by remote sensing, for example by DIAL or LIF. Instead of probing ambient levels of key free radicals, a study of the relaxation kinetics in real time enables chemical mechanistic studies *in situ*.

I. INTRODUCTION

For some key species such as tropospheric OH, the *in situ* measurement of its concentration is a difficult problem. One possible way of gaining information on OH radical reactions in the real troposphere has recently been proposed: Pump-and-Probe LIDAR [1]. In this relaxation technique, which is by no means restricted to the measurement of OH, an intense light pulse perturbs the atmosphere. Subsequently the return of [OH] to its steady-state value is observed by optical remote sensing techniques such as DIAL or long path absorption.

The central idea of the Pump-and-Probe LIDAR is to combine the time resolution of the flash photolysis with the spatial resolution of the LIDAR technique to what can be called a real-time *in situ* spatially resolved atmospheric chemical kinetics field experiment. The emphasis is placed on the verification and completion of the **chemical mechanisms** operative under given atmospheric conditions. In a later phase transport in and out of the irradiated volume will be considered. To test the feasibility of such a Pump-and-Probe LIDAR we have numerically simulated the experiment, and this is the subject of the present work.

We have modeled the following four scenarios: In **scenario A**) a (hypothetical) pump pulse bleaches NO₂ at $\lambda < 399$ nm in order to "inject" an equivalent quantity of O(³P) whose decay with time is calculated together with all the other chemical species directly affected by it. In **scenario B**) a model troposphere is perturbed by a powerful pump pulse from a KrF excimer laser at 248 nm which flash photolyzes O₃ to give O(¹D) and O₂(¹D). The electronically excited oxygen atoms insert into H₂O thus generating a transient high concentration of OH radicals. Quenching processes generate significant amounts of O(³P) which is the reason we had to include scenario A. In **scenario C**) a powerful pump pulse at 308 nm generates H from photolysis of H₂CO and OH from photolysis of O₃ in an unpolluted troposphere rich in CH₄ and H₂CO. In **scenario D**) both H and OH are generated by

two-photon photodissociation of H₂O at 248 nm at high laser powers. We stress that the present effort relates to the chemical aspect of the troposphere only. Therefore, the necessity of having to include transport properties under given meteorological conditions will be given by its chemical lifetimes which is the primary subject of this paper.

II. METHOD OF CALCULATION

A simplified chemical model of the troposphere including 76 chemical species and 166 reactions was treated using the CHEMKIN II package of programs [2]. This flexible set of programs was chosen because it incorporates the temperature and pressure dependence of all uni-, bi- and termolecular reactions. CHEMKIN II explicitly takes into account the reverse of every elementary reaction. This aspect is important for chemical equilibria such as N₂O₅ \rightleftharpoons NO₃ + NO₂ or CH₃C(O)O₂NO₂ (PAN) \rightleftharpoons CH₃C(O)O₂ + NO₂ where the adduct is weakly bound and where its lifetime thus varies significantly in the temperature range of interest. Most kinetic parameters were taken from kinetic data evaluations for atmospheric chemistry [4] or were estimated [3]. The calculated steady state concentrations for these different tropospheres are given in Table 1.

III. RESULTS AND DISCUSSION

Several different ways of perturbing the atmosphere were considered: The reactions NO₂ + h ν \rightarrow NO + O(³P) (scenario A) and O₃ + h ν \rightarrow O₂(¹D) + O(¹D) (scenario B) are equivalent to a burst or an instantaneous "injection" of O(³P) and O(¹D), respectively. It leads to transient atom concentrations which are as high as the steady state NO₂ and O₃ concentrations. This has dramatic consequences on other key species as shown below in terms of their relaxation rate. A different type of perturbation is introduced when H atoms are injected into the atmosphere through photolysis of H₂CO (scenario C) or two-photon dissociation of H₂O (scenario D)

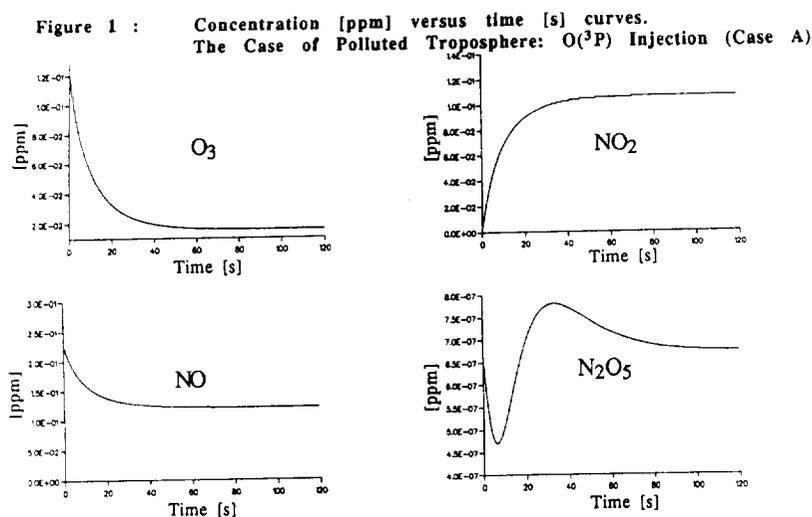
Scenario A) Case of Polluted Troposphere: O(³P) Injection

At time $t=0$ a short laser pulse at $\lambda < 398$ nm is assumed to completely bleach NO₂. The degree of bleaching depends on the laser beam fluence and the excitation wavelength. Complete bleaching of NO₂ is difficult to attain but is assumed here in order to simulate that portion of O(¹D) that is converted to O(³P) through collisional quenching of O(¹D) (see scenario B). Figure 1 below shows the recovery/relaxation of O₃, NO₂, N₂O₅, and NO. The recovery of NO and NO₂ is related to the presence of O₃, and

Table : Typical Steady-State Levels of Trace Gas Constituents

Species	Steady State Concentration ¹⁾ [ppm] Polluted Atmosphere	Steady State Concentration ¹⁾ [ppm] Unpolluted Atmosphere	Steady State Concentration ¹⁾ [ppm] Unpolluted Atmosphere - High Level of CH ₂ O
NO	0.121	0.658×10^{-2}	0.226×10^{-4}
NO ₂	0.107	0.493×10^{-2}	0.129×10^{-3}
N ₂	0.772×10^6	0.772×10^6	0.772×10^6
N ₂ O ₅	0.671×10^{-6}	0.206×10^{-7}	0.148×10^{-8}
O ₂	0.208×10^6	0.208×10^6	0.208×10^6
O ₃	0.0157	0.0133	0.0533
H ₂ O ²⁾	0.198×10^5	0.198×10^5	0.198×10^5
CO	0.872	0.198	0.248
CO ₂	0.346×10^3	0.346×10^3	0.346×10^3
CH ₄	1.480	1.480	1.480
C ₂ H ₄ ³⁾	0.247	0.953×10^{-2}	0.334×10^{-2}
C ₄ H ₁₀ ³⁾	0.247	0.967×10^{-2}	0.990×10^{-2}
HONO	0.402×10^{-4}	0.363×10^{-4}	0.106×10^{-5}
HNO ₃	0.372×10^{-2}	0.673×10^{-3}	0.304×10^{-2}
H ₂ O ₂	0.472×10^{-12}	0.276×10^{-10}	0.440×10^{-2}
CH ₂ O	0.414×10^{-2}	0.464×10^{-3}	0.982×10^{-2}

- 1) The Zenith Angle of the sun was 30° at midlatitudes
- 2) Relative Humidity of 60% at 300K and 1013 mbar
- 3) C₂H₄ and C₄H₁₀ are representative of all the NMHC.



occurs on the time scale of several seconds, which is also the time scale of NO₂ photolysis by sunlight. The decay of O(³P) occurs on a very short time scale of several tens of microseconds according to $O + O_2 \rightarrow O_3$. The interesting concentration vs. time-curve for N₂O₅ is due to (sequentially): the disappearance of NO₂ by the pump pulse, oxidation of NO₂ to NO₃ by O₃ resulting in an excess of N₂O₅, and finally relaxation to the steady state levels of NO₂ and NO₃.

Scenario B) Case of Unpolluted Troposphere: O(¹D) Injection

At time $t=0$ a short laser pulse of about 300 mJ/cm² at $\lambda=248$ nm completely bleaches O₃ to O₂(¹D) + O(¹D). The latter generates OH free radicals by insertion into H₂O or O(³P) by collisional quenching with air. The maximum OH concentration corresponds to 10¹¹ molec/cm³ which is an enhancement of 2×10^6 above the steady state concentration.

Low levels of NO_x lead to a significantly longer lifetime of OH (150 ms, Figure 2) compared to a polluted troposphere (7 ms). Surprisingly, the OH density is lingering on for several seconds at levels which are readily observable by DIAL. This "delayed" formation of OH results from the reaction of HO₂ + NO + OH + NO₂ during the HO₂ peak due to CH₄ oxidation by OH ($CH_3 + CH_3OO + CH_3O + HO_2 + H_2CO$). Methane is thus the true precursor of this "delayed" OH. The OH and CH₃ density vs. time curves track each other as do CH₃O₂ and HO₂.

Scenario C) Case of Unpolluted Troposphere: H and O(¹D) Injection

An intense laser pulse of 300 mJ/cm² at 308 nm generates 2×10^9 H atoms/cm³ due to photodissociation of 10 ppb of H₂CO and subsequent reaction of HCO with O₂, as well as to 4×10^9 OH due to O₃ photolysis. The lifetime of H is extremely short and leads instantly to HO₂. Figure 3 displays the response of an unpolluted troposphere with low levels of

Figure 2 : Concentration [ppm] versus time [s] curves.
The Case of Unpolluted Troposphere: O(¹D) Injection (Case B)

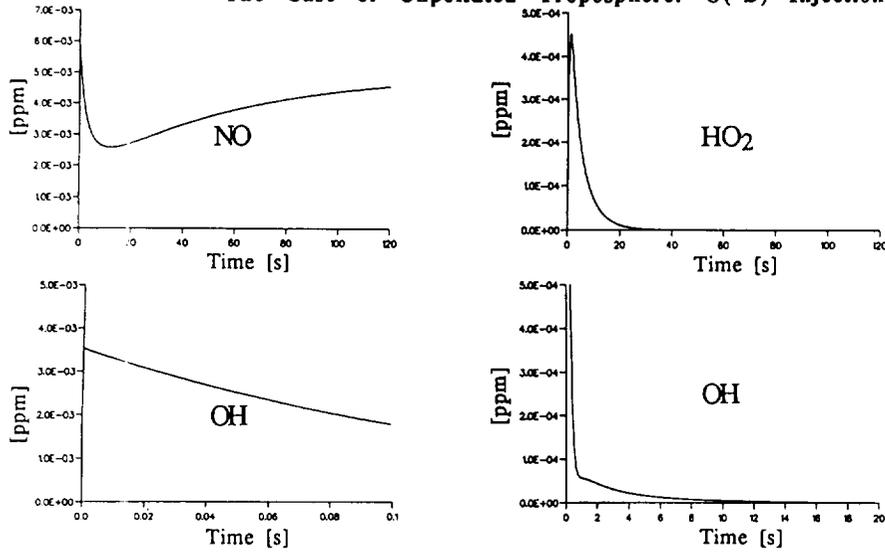


Figure 3 : Concentration [ppm] versus time [s] curves.
The Case of Unpolluted Troposphere (except for high level of CH₂O):
H and O(¹D) Injection (Case C)

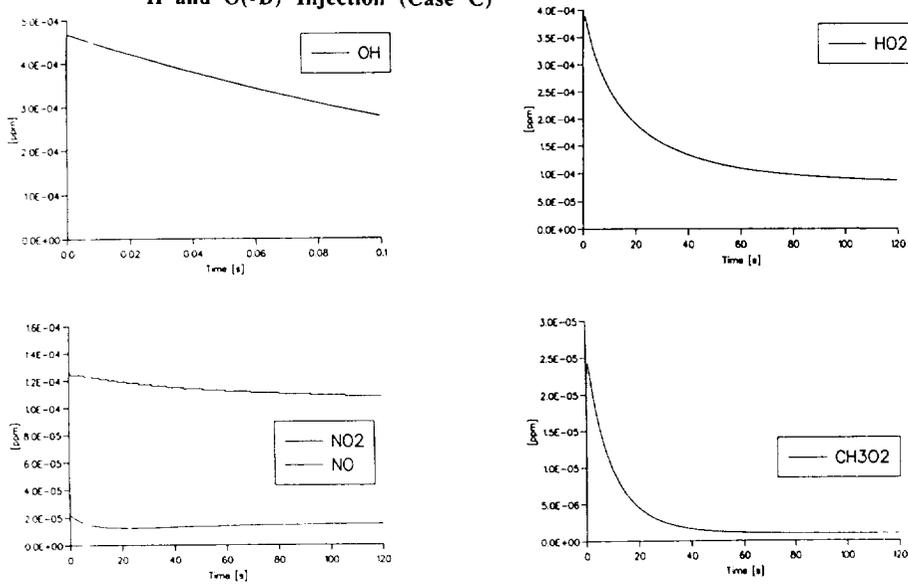
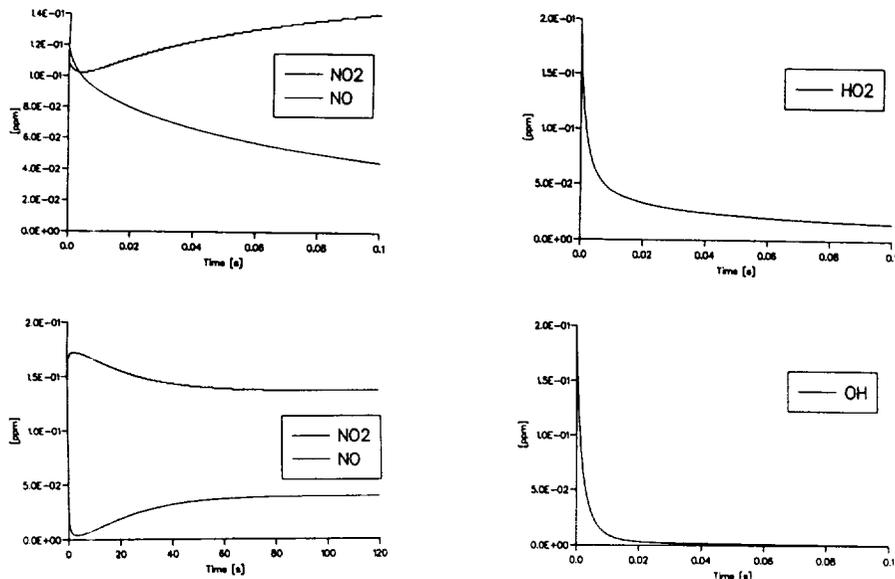


Figure 4 : Concentration [ppm] versus time [s] curves.
The Case of Polluted Troposphere : H and OH Injection (Case D)



NO_x . The OH decays with a time constant of 190 ms, whereas the HO_2 increases from the initially generated level to a maximum at 1 s, mainly because of the reaction $\text{OH} + \text{H}_2\text{CO}$ and $\text{OH} + \text{H}_2\text{O}_2$. The low level of NO in this atmosphere enables the high concentrations of HO_2 and CH_3O_2 . The interaction of two HO_2 affords H_2O_2 that photolyzes into OH which in turn attacks more hydrogen peroxide thus providing a steady source for more HO_2 . The low level of NO and the slow photolysis of H_2O_2 are at the origin of the longevity of HO_2 at elevated concentrations in analogy to the long-lasting OH from scenario B).

Scenario D) Case of Polluted Troposphere: H and OH Injection.

High power laser radiation at 248 nm may lead to two-photon photolysis of atmospheric water vapor to $\text{H} + \text{OH}$. We have assumed the extent of the H_2O photolysis to be around 10 ppm of the water vapor (upper limit). Figure 4 displays the response of the polluted atmosphere in which the OH and HO_2 levels initially decay at the same rate to result in the regeneration of H_2O . Due to its high reactivity the OH decays to a larger extent, so that the increased level of HO_2 interacts with the high levels of NO albeit on a much shorter time scale compared to scenario C). At later times the NO and NO_2 levels reach their photostationary state. The peak in NO_2 is due to the reaction $\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}$ which leads to a related maximum in O_3 , which in turn is responsible for much of the secondary chemistry at later times.

IV. CONCLUSIONS

→ The relaxation/recovery can occur on very different time scales according to the strength of the perturbation, scenario C) vs. D) or the species observed, for instance OH vs. NO, scenario B).

→ For one observed species different elementary reactions can be important at different times after the relaxation, for instance see N_2O_5 , scenario B).

→ Several transient species may be detected during the recovery of the system back to steady state, for instance OH ($10^{11} \text{ molec cm}^{-3}$) or HO_2 ($10^{10} \text{ molec cm}^{-3}$) using state-of-the-art detection techniques..

→ Several modes of laser-perturbation lead to direct insight into the hydrocarbon oxidation cycle in the aftermath of a powerful pump pulse under low NO_x conditions, even using a relatively simple reaction mechanism.

→ Radical-radical reactions can become important in the aftermath of the perturbing pulse due to large transient densities of free radicals. For instance $\text{OH} + \text{HO}_2$, scenario D) or $\text{HO}_2 + \text{HO}_2$, scenario C). This interaction is emphasized even more under low NO_x conditions.

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